The Hot Bands of Methane between 5 and 10 μm
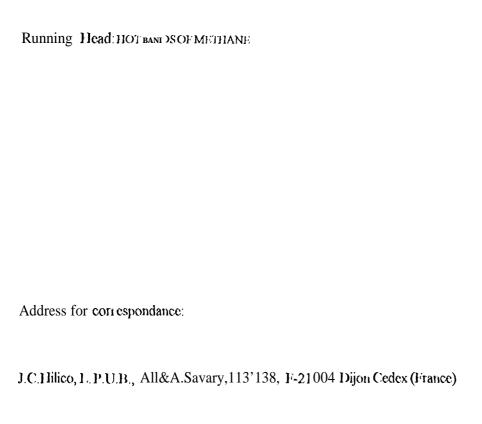
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ABSTRACT

Experimental line intensities of 172.7 transitions arising from nine hot bands in the pentad-dyad system of methane are fitted to first and second order using the effective dipole moment expansion in the polyad scheme.. The observed bands are v_3-v_2, v_3-v_4, v_1-v_2, v_1-v_4, $2v_4$-v_4, v_2+v_4-v_2, v_2+v_4-v_4, $2v_2$-v_2, and $2v_2$-v_4, and the intensities are obtained from long-path spectra recorded with the Fourier transform spectrometer located at Kitt Peak National Observatory. For the second order model, some of the 27 intensity parameters are not linearly independant, and so two methods (extrapolation and effective parameters) are proposed to model the intensities of the hot bands. In order to obtain stable values for three of these parameters, 1206 dyad (v_4,v_2) intensities are refitted simultaneously with the hot band lines, The simultaneous fits to first and second order lead to rms values, respectively of 21. 5o/o and 5.0°/o for the 1727 hot band lines and 6.5% and 3.0% for the 1206 dyad lines.

The. band intensities of all 10 pentad-dyad hot bands are predicted in units of $cm^{-2} atm^{-1}$ at 296 K to range from 0.931 (for $2v_4$-v_4) to 7.67 x 10^{-5} (for $2v_4$-v_2). The total intensities are also estimated to first order for two other hot band systems (octad-pentad and tetradecad-octad) that give rise to weak transitions between S and 10 μm

INTRODUCTION

At room temperature and in equilibrium conditions, the vibrationally excited levels of methane with non-negligeable populations arc the levels (v_4 1; 1310 cm^{-1}) and (v_2 1; 1530 cm^{-1}) which correspond to the two bending vibrational modes of the molecule. To zero order of approximation, the vibrationally-induced dipole moment for methane has two components which arc nearly equal ($\approx$0.1 Debye) and opposite in sign These moments are associated with the two fundamental infrared active modes having F_2 symmetry: μ_3 for v_3 near 3020 cm^{-1} and μ_4 for v4 near 1310 cm^{-1}. Thus, at room temperature, the four strongest hot bands of methane arc expected 10 be 2v4-v4 and v_2+v4-v_2 near 1300 cm^{-1} and v_3+V4-V4 and v_2+v3-v_2 near 3000 cm^{-1}. If one supposes that all the upper and lower state energies are known through the line positions of transitions arising from the ground state, then the full prediction of the hot bands requires only the correct modeling of line intensities,

Early attempts to reproduce hot band intensities were hindered by the lack of experimental data and incomplete theoretical knowledge. In 1978, Pascaud et al. (1) did the first study of a methane hot band, They predicted the relative int ensities of v_3-v_4 using the isolated band scheme with the spherical formalism and the first order vibrational (in q_3q_4) dipole parameter. In a preliminary study of 2v_4-v_4 and v_2+v_4-v_2 in 1980, Pierre et al. (2) employed isolated band models in both the spherical and tetrahedral tensorial formalisms using just the zero order μ_4 dipole moment parameter. However, without reliable observed intensities, they could only produce a relative intensity prediction somewhat normalized to the apparent v4 strengths. Finally, in 1981 Hunt et al.

(3) and Brown et al. (4) tabulated measured intensities of $\nu_3\text{+}\nu_4\text{-}\nu_4$ and $\nu_2\text{+}\nu_3\text{-}\nu_2$, respectively, but they did not attempt to model these data.

After these studies, important progress was made in methane spectroscopy. Firstly, a new theoretical understanding evolved from the generalization of the polyad scheme to the tetrahedral formalism by Champion (S) and from the introduction by 1 .octe (6) of a general development of the effective dipole moment operator adapted to the tensorial and computational techniques. The theory of ambiguities initiated by Perevalov et al. (7) was also applied to the different polyads, and its implications about the determination of intensity parameters was understood as well (8). This well-established theory was reviewed by Champion et al. (9). Secondly, comprehensive and accur at e experimental positions and intensities were obtained using the Kitt Peak Fourier transform spectrometer in the 1.6 to 9 μm regions (see Brown et al. (10) and the refer ences therein). These new data permitted the advanced theoretical schemes to be validated In Brown et al. (11), the 1206 transitions of the ν_4 and ν_2 dyad were reproduced with an rms of 3% while in Hilico et al, (1.2)413 lines of ν_3 - V_4 were fitted to 40A, Some theoretical expressions were givenby1acte(13) to define relat ionships bet ween dipole moment parameters, and in a simult aneous study of $\nu_2\text{+}\nu_3$ and $\nu_3\text{-}\nu_2$ (14), these were confirmed by predicting the band strength of the hot band within 4% of the observed value. These same expressions wer e used by Oldani et al. (15) and Hilico et al. (16) to predict the rotational and the dyad - dyad spectrum bet ween O and 579 cm^{-1}.

The present paper describes the analysis of the pentad-dyad intensities. Six of the ten bands were first considered by 1 .octe in his thesis (17) to illustr ate the power of the theory. Later, Ouardi (18) undertook the complete study in the polyad scheme covering the transitions in the 1100 to 1900 cm^{-1} region observed with the Kitt Peak FTS, and a prediction of the nine bands were included in the 1992} HTRAN database (see Brown et al.(1 O)). However, the thesis study used older energy level analyses which were later refined using an Hamiltonian operator developed to sixth order for the dyad (19) and to fourth order for the pentad (20). In these new studies, the ambiguities of the

Hamiltonian were completely reduced to fifth order in the d yad case and to third for the pentad part. These reductions are coherent in so far as the ground state and dyad parts of the effective pentad Hamiltonian used in Ref. (20) is *exactly* the effective Hamiltonian of Ref. (19). Thus, in the present paper we have merged new and prior (11,18) intensity measurements and refitted nine hot bands with the two fundamentals in order to obtain an improved set of pentad-dyad intensity parameters consistent with the best available energy level studies

THEORY FOR HOT BAND STRENGTHS OF TETRAHEDRAL MOLECULES

The theoretical background for modeling the energy spectrum as well as transition moments of methane, is detailed in Ref. (9). Due to Coriolis and Fermi resonances, the polyad scheme for methane consists in successive clusters: Vibrational ground state (g.s.), dyad (v_2 and v_4), pentad ($2v_4$, $v_2 + v_4$, $2v_2$, v_1 and v_3), octad ($3v_4$, $v_2 + 2v_4$, $2v_2 + v_4$, $3v_2$, $v_1 + v_2$, $v_1 + v_4$, $v_2 + v_3$, and $v_3 + v_4$), tetradecad and so on. In the tetrahedral formalism, any rovibrational operator as well as the effective transition moment or contact transformation operator is written in tensorial form:

$$O = \left[R^{\Omega(K,n\Gamma)} \times^{\varepsilon} V \begin{array}{ccc} \Gamma_1 & \Gamma_2 & \Gamma_v \\ \{n_s\} & \{m_s\} \end{array} \right]^{(C)} \tag{1}$$

$\{n_s\} = n_1, n_2, n_3, n_4$, (respectively $\{m_s\} = m_1, m_2, m_3, m_4$) corresponds to the number of annihilation (respectively creation) operators associated to each mode and used to build the vibrational part of O. Γ and C are tetrahedral symmetry species associated to the different operators. C is A_1 for any Hamiltonian or contact transformation operator and F_2 for the effective dipole moment (in the molecular frame). At this stage., it can be emphasized that occurrence of rotational operators in the effective dipole development is the consequence of the contact transformation implicit l y applied to separat e the chosen polyads and to reduce ambiguit ics inside polyads. Using the

projection technique, the effective Hamiltonian for an excited state includes a sum of operators associated with the lowest polyads. This constitutes the basis of the extrapolation method commonly applied to study upper polyad energy levels. For instance, the effective pent ad Hamiltonian can be written:

$$H^{(Pentad)} = H^{(Pentad)}_{\{G.S.\}} + H^{(Pentad)}_{\{Dyad\}} + H^{(Pentad)}_{\{Pentad\}} \qquad [2]$$

where the lowest indices correspond to a given type of vibrational operator, characteristic of this polyad and the upper indices to the projection space. The same kind of projection can be applied to the effective dipole operator for hot bands, In the case of interest here (pentad-dyad), the effective dipole can be written:

$$\mu^{(Dyad,Pentad)} = \mu^{(Dyad,Pentad)}_{\{G.S.,Dyad\}} + \mu^{(Dyad,Pentad)}_{\{Dyad,Pentad\}} \qquad [3]$$

to be compared with the expression of the effective dipole for the dyad-g.s. transitions:

$$\mu^{(G.S.,Dyad)} = P^{(G.S.,Dyad)}_{\{G.S.,Dyad\}} \qquad [4]$$

Here the double lower indices corresponds to the vibrational types of the lower and upper state. Each term in Eq. [3] or [4] is a linear combination of operators like Eq. [1], which, as explained in Ref. (9), can be classified by order of magnitude according to Aliev and Watson (21). Table 1 lists the 27 operators for the second order development of the effective (pentad-dyad) dipole operator. All useful indices are given (nl' has been replaced by 1', n being always O in the present case) and operators arc classified by vibrational type as in Eq. [3], then by order of approximation and composition, Operators with a rotational part in $0(0,A_1)$ are pure vibrational operators and their typical composition is given in the last column. Operators with $1(1,F_1)$ rotational part give 'Herman-Wallis' corrective contributions to the corresponding pure vibrational ones. The first seven operators (# 1 to 7) associated with dyad-g.s. are exactly those already used in the second order linestrength analysis of the dyad (11) (although they are listed in slightly different order). To obtain the operators associated to one laboratory component of the effective dipole moment, it is necessary

to combine the molecular components (tensor of symmetry F_2) with the direction cosine tensor (conventional symmetry F_1) to obtain, in tensorial form:

$$^{(lab)}\mu^{(A_2)} = \left[C^{(F_1,F_1)} \times ^{(mol)}\mu^{(F_2)} \right]^{(A_2)}$$

[5]

where $^{(mol)}\mu^{(F_2)}$ has the form of Eq. [1], The tensorial product in Eq. [5] must be symmetrized because the two factors do not commute in general. Finally, matrix elements, in the coupled tetrahedral basis, of any operator of the effective dipole moment is given by:

$$_{(}J,n_r,C_r;\{v_s\},C_v;C,\sigma \quad O^{(A_2)} \quad J',n'_r,C'_r,;\{v'_s\},C'_v;C',\sigma'_) =$$

$$\frac{3}{2} F^{A_2 C C}_{\sigma'\sigma} [C] \langle J \| C^{(F_1)} \| J' \rangle \left\langle \{v_s\},C_v \| ^{\varepsilon}V^{\,l_1\quad l_2\quad l_v}_{S\{n_s\}\{m_s\}} \| \{v'_s\},C'_v \right\rangle$$

[6]

$$\times \left\{ A \langle J \| R^{\Omega(K)} \| J \rangle + B \langle J' \| R^{\Omega(K)} \| J' \rangle \right\}$$

where:
$$O^{(A_2)} = \left[CC^{(F_1,F_1)} \times \left[R^{\Omega(K,nT_r)} \times ^{\varepsilon}V^{\,l_1\,l_2\,l_v}_{\{"s\}\{\%\}} \right]^{(F_2)} \right]^{(A_2)}$$

F is a Clebsh-Gordan coefficient in the T_d group, $[C]$ the dimension of the irreducible representation C and $\langle . \| . \| . \rangle$ are reduced matrix elements. A and B are functions of 12-C recoupling coefficients and isoscalar K coefficient for the chain $O(3) \supset T_d'$, namely:

$$A = \sum_{n'',C_r} \begin{Bmatrix} \Gamma_r & \Gamma_v & F_2 & A_2 \\ C_r & C_v & C & C'_r \\ C''_r & C'_v & F_1 & C' \end{Bmatrix} \quad K^{\,1_g\quad J'_g\quad J_g}_{F_1\, n'C_r\, n''C''_r} \quad K^{\,K\quad J_g\quad J_g}_{\Gamma_r\, n''C''_r\, nC_r}$$

[7]

$$B = (-1)^{J'+J+C'_r+C_r+C'_v+C_v+C'+C+\Gamma_r+\Gamma_1} \sum_{n'',C_r} \begin{Bmatrix} \Gamma'_r & \Pi_v & F_2 & A_2 \\ C'_r & C'_v & C & C'_r \\ C'_r & C_v & F_1 & G \end{Bmatrix}, \quad K^{\,1_g\quad J'_g\quad J_g}_{F_1\, n'C_r\, n_rC_r} K^{\,K\quad J'_g\quad J'_g}_{\Gamma_r\, n'C'_r\, n''C''_r}$$

[8]

Selection rules reduce to $\Delta J = 0,\pm 1$, and $A_1 \longleftrightarrow A_2, E \longleftrightarrow E$ and $F_1 \longleftrightarrow F_2$. As the Hamiltonian is diagonal in J and C, one can consider now the (J, C; J', C') part of the dipole matrix, supposing that the tetrahedral basis functions are sorted according to the vibrational sublevels in each polyad. The

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block structure of the matrix has 18 partitions (2 sublevels in the dyad and 9 sublevels in the pentad), as illustrated in Table 2. Among the 20 rovibrational operators in $\mu^{\langle Dyad, Pentad \rangle}_{\{Dyad, Pentad\}}$, there are 17 different vibrational parts and, by construction, their reduced matrix elements are 1 for one specific block and O for all others, This is illustrated in Table 2 for the operators associated with v_2+V_4-v_2 and $2v_4$-v_4 (#18-19 and /)2 S-27, respectively, in l'able 1). For the $\mu^{\langle Dyad, Pentad \rangle}_{\{G.S., Dyad\}}$ part, there are only two different vibrational operators and their reduced matrix elements are also given in Table 2. A close examination of Eqs. [6-8] shows that matrix elements of operators with the same tensorial characters $(\Omega(K,\Gamma), \Gamma_v, 1^{\cdot})$ in a given block with (J, C_v, C; J', C'., C') are exactly proportional, and the proportionality coefficient is simply the ratio of their vibrational reduced matrix element (when different from zero). In the case of the (pentad-dyad) problem, this situation arises precisely for the set of six operators (#1,18,19,25,26,27 in 'fable 1), with Γ_v= F$_2$, and only for this set. The consequence of this proportionality y, specific to hot band transition moments, is a linear dependence between the operators, that makes it impossible to determine the associated parameters by a least square procedure on the basis of only hot band strength measurements. Returning to the present case shown in Table 2, all ($2v_4$-v_4) and (v_2+v_4-v_2) operators arc linearly independent by construction; then only one linear condition exists, connecting the main zero order parameter (p_i in Table 1) and the five second order parameters given in Table 2. This problem of dependence appears only for the second order model and in this case, three strategies can be (and have been) applied:

a) *The extrapolation method*: the seven d yad parameters arc fixed (including p_1) to the values obtained first by the. dyad second order analysis and one determines only the values of the 20 (pentad-dyad) parameters by a fit of hot band strengths.

b) *The method of e..fictivc parameters:* the main p_1 parameter is suppressed (or fixed to zero) and its contribution is absorbed by the other five ($2v_4$-v_4) and (v_2+v_4-v_2) parameters which become

effective parameters determinable (with other parameters) by the fit of hot band strengths If p'_i is the effective parameter corresponding to the original p_i, one obtain using numerical values of Table 2:

$$p'_{18} = p_{18} + p_1$$

$$p'_{19} = p_{19} + p_1$$

$$p'_{25} = p_{25} \sqrt{\tfrac{2}{3}} p_1 \qquad\qquad [9]$$

$$p'_{26} = p_{26} - \tfrac{2}{\sqrt{3}} p_1$$

$$p'_{27} = p_{27} - \sqrt{2} p_1$$

Even if the other dyad parameters are not connected by linear dependence, it seems physically reasonable to fix them (as in extrapolation method) to their dyad obtained values..

c) *The simultaneous analysis method*: All 27 parameters are adjusted simultaneously to fit the dyad and hot band data so that dipole moment parameters can be determined without theoretical restriction,

ANALYSIS OF (PENTAD-DYAD) HOT BAND STRENGTHS

1. Preliminaries

In this section, the analyses of pentad-dyad and dyad-g.s. intensities, using three different orders of magnitude and three different analysis strategies are presented. In the previous dyad strength analysis (11), the adjusted quantity was the matrix element of the dipole moment operat or, a linear combination of the dipole parameters. Its absolute value is proportional to the square root of the measured strength and its sign was calculated This linearization avoids iterative process in the least square method, but it supposes that the zero order term is dominant for all lines in order to

determine theoretically the sign of matrix elements, This assumption cannot be verified for all lines in the (pentad-dyad) problem For instance, ν_3-ν_4 linestrengths are dominated by the first order parameter (p_{10}) associated with this band rather than by p_1 (associated to ν_4). So, for the hot band study, the more general nonlinear least square iterative method has been applied, As this study cannot be separated from the dyad one, the 1206 dyad linestrengths already selected and used in Ref. (11) have been reanalyzed with the same iterative method to provide self consistent comparisons.

The different methods described before have been used for the dipole moment development to order O, 1, 2. In each case, the dyad strengths were reanalyzed to the same order, separately and simultaneously in view of comparison of obtained parameters. To estimate the quality of the different fits, we use the *relative weighted standard deviation* with the following precise definition: if S_{exp} is the measured strength of one given line and if $5,\$,,1$ is its experimental relative accuracy (in %) which has been determined by comparison of different measures or which has been estimated by some minimum, the absolute precision on S_{exp} is $\delta S_{obs} = S_{exp} \times \delta S_{rel}$. In the least square process, the weight associated to S_{exp} is $w = 1 / \delta S_{obs}$. Then, the relative weighted standard deviation σ is defined by: $\sigma^2 = \dfrac{\sum_i w_i \Lambda_i^2}{\sum_1 w_i}$,where $\Lambda_i = (S_{exp} - S_{calc})/S_{exp}$ is the *relative* deviation.

So, the minimized quantity σ is very sensitive to weigths, i.e. to the estimation of relative accuracy of strength measurements. To compare the present results with previous ones, the simpler rms based on $A_i = (S_{exp} - S_{calc})/S_{exp}$ will be also given

2. Selection of experimental data

All the spectra were recorded between 1979 and 1990 with the Fourier Transform spectrometer located at the McMath telescope at Kitt Peak National Observatory/ National Solar Observatory. Two matched He-cooled Ar-doped Si detectors were used with six different absorption cells whose optical paths ranged from 0.027 m to 433 m The same spectra were also used for the dyad and $\nu_3-\nu_2$ studies and are described in detail in Refs. (1]) and (14), The selection of hot band lines was based on coincidences between observed and predicted frequencies from the dyad (19) and pentad (20) positions results, The intensities obtained in interim predictions were also used to distinguish these weak lines from the so called forbidden lines of the. dyad and from the dyad $^{13}CH_4$ lines present in natural abundance (positions(19) as well as intensities (11) of the $^{13}CH_4$ dyad being known with confidence). The choice of isolated hot band lines was made possible by the complete knowledge of the methane spectrum in the 5-10 μm region At the end of the analysis, a good prediction based on data from six hot bands was used to seek transitions of the other four hot bands; three were located, and over intensities of nearly 1000 transitions were added to the prior data, Finally 1732 hot band measured lines were selected after several iterations The lines were assigned to nine of the ten pentad-dyad bands with the number of assignments ranging from 691 for $\nu_3-\nu_4$ to only 11 for $\nu_1-\nu_2$. The highest J value is 16, it corresponds to lower energy levels as high as 3000 cm^{-1}. The hot band intensities ranged in units of $cm^{-2} \cdot atm^{-1}$ at 296 K from 1.x1 0^{-2} to 7.x10^{7} compared to a range of 2.4 to 2.x105 for the dyad lines. Because the hot band lines are weaker and more sensitive to temperature uncertainties, the experimental accuracies of the hot bands lines were assumed to be larger than those of the dyad. in the fits of the dyad measurements, the same uncertainties (with a minimum of 1. so/o) already used in Ref (11) were applied. For hot band lines, the minimum has been fixed to 3% (for 1431 lines), other lines having an error from 3 to 26%, which was statistically determined from 2 to 4 different measures as explained in details in Ref.(11) For 83 weakest lines measured only once, the relative accuracy was fixed to 10°/0,

3. Order zero

Even if order zero is known to be inadequate in the dyad case, it is instructive to compare how much the simple model diverges for the dyad and hot bands. To zero order of approximation, only one dipole parameter (p_1 in 'fable 1 or μ_4 in introduction) is involved for the dyad as well as the hot bands. The obtained values for this parameter arc 8.654(29) 10⁻2 Debye for the dyad with $\sigma = 36.6°/0$ for 1206 data and only 2.062(84) 10-2 D for hot bands with $\sigma = 93,8°$A for 1732 data, A simultaneous fit of both sets of linestrengths leads to a value of 2, 888(70) 10-2 D and worst results for σ (86.4% for the dyad and 103 .5% for hot bands!). The fact that separate values for $p_1 = \mu_4$ are so different shows that simple extrapolation from the dyad to the (pentad-dyad) system cannot produce satisfactory results and the necessity to use a higher order development for the dipole moment operator.

4. Order one

To illustrate the case for the first order approximation, the six dipole parameters required are shown in Table 3 along with corresponding values obtained by different methods, The first three apply to both the dyad and hot bands while the last three pertain only to the hot bands, The six parameters are independent and can in principal be determined from only the hot band data (5th column of Table 3). Parameters can also be obtained with the extrapolation method by fixing the first three dyad parameters to values obtained by fitting the dyad intensities (3rd column) and adjust ing the other three using the hot band data (4th column of Table 3) or with the simultaneous fitting of dyad and hot band data to adjust all six parameters (last column of Table 3). All the relative standard deviations are of the order of 40°/0 for the fitted hot band data, The very large value (868°/0) obtained for the hot band lines from the three dyad parameters shows again that a

simple extrapolation (without new parameters) from the dyad cannot give a good prediction of hot band linestrengths, even to order one. If one is interested only by hot bands, the best fit (0-40.2%) restricted to hot band lines is obtained with six free parameters, but in this case the three dyad parameters are significatively different from their dyad value and the corresponding σ increases from 8.4'% to 20.77.. Finally, the extrapolation method (i.e. fit of hot band lines with only the three (pentad-dyad) free parameters) or the simultaneous fit of all data with all parameters give results which are comparable (even if the obtained values for the parameter p_2 are different). A band by band examination of the results shows that the large global value ($\sigma \approx 40\%$) is mainly due to the weak band $2v_2-v_4$ (7 S^0/.) and 6 weak lines of v_1-v_4 (probably because of the. Fermi resonance between $2v_2$ and v_1). Suppressing these 6 lines and all the 92 lines of $2v_2-v_4$ and with exactly the same parameters, one obtains a global standard deviation of 2 1%, (with a better distribution, from 10% to 310/., among the eigth remaining bands) and the corresponding rms of 11-13% are more acceptable, This observation shows that the first order model, with only three hot band parameters, associated with v_1-v_4, v_3-v_2 and v_3-v_4, is not sufficient to reproduce intensities of other weakest hot bands.

5. Order two

To second order of approximation, there are 27 parameters in the complete development of the effective dipole moment operator for the (pentad-dyad) system, seven of which are already used for the (dyad-g.s.) intensities, First, a new fit of the 1206 dyad data gives new values of these seven parameters. If all seven parameters are free, the present obtained value for the parameter p_5 (named ^{2}1$ in Ref. (1.1) is 0.61 10^7D with a standard deviation of 1.7107 D. This parameter which is strongly correlated with p_1 (as explained in details in Ref. (1 1) is statistically non- significative, and it

was fixed to zero without any deterioration of the fit, Results arc reported in Table 4, The rms of 3.0% is comparable to the value (2.9%) reported in Ref. (11) and obtained with another least square algorithm The extrapolation to hot bands with only these seven parameters leads to results as worst as for order one.

As explained before, the usc of hot band data alone does not produce good results if all 27 parameters are freely adjusted. Therefore, the extrapolation and the 'effective parameter' methods were used to fit the hot band data, In both cases, all seven dyad parameters were fixed, In the first method, p_1 (which is linearly dependent of pig, $p_{19}, p_{25}, p_{26}, p_{27}$) was fixed to its dyad value, the other five parameters being second order corrections for $v_2 + v_4 - v_2$ (p_{18}, p_{19}) and $2v_4 - v_4$ (p_{25}, p_{26}, p_{27}). In the second case, p_1 was fixed to zero and the obtained values for the other five parameters are effective values ($p'_{18}, p'_{19}, p'_{25}, p'_{26}, p'_{27}$) of Eq. [9]. In both cases, other six dyad parameters were fixed to their dyad values. Results are also reported in Table 4, With exception of the set of five effective parameters, the numerical obtained values of other hot band parameters are *exactly* the same, with the same precision. Line by line deviations are also identical so that the two methods are equivalent. Of course Eqs. [9] are exactly verified, as expected by theory (this is a good check for numerical programs). Finally, the 27 parameters can be determined if both dyad and hot band data arc fitted simultaneously; their values appear in last column of Table 4. In the simultaneous fit, the parameter p_5 becomes more significative and it was let free, Statistically, the zero order parameter p_1 is determined by both dyad (52%) and hot band (48%) data whereas other dyad parameters are determined mainly (76 to 98%) by the dyad data. Of course, hot band parameters depend only on hot band data. If one compares the values resulting from the simultaneous fit with those resulting from extrapolation, i.e. from separate fits, it can be seen that all confidence intervals have the same order of magnitude with the exception of parameters p_{20} and p_{21} respectively associated to $2v_4 - v_2$ (missing band) and $2v_2 - v_4$. On the other hand, some second order parameters (p_{18}, p_{20}, p_{21} and p_{23}) have very different values. It was shown numerically that these differences

disappear if the simultaneous fit is done with p_5 fixed to zero; in this situation, one obtains for all 26 remaining parameters values and precision very close to those resulting from the extrapolation method and an equivalent standard deviation of So/O (instead of 6,6°/0 with $p_5 \neq 0$). So hot band results are very sensitive to this second order dyad parameter which was statistically undeterminable from the only dyad data. On the basis of the present dyad and hot band data, the parameters appearing in the last column, of Table 4 can be considered as the best ones. The list of fitted data and their residuals can be obtained from one of L.P.U.B. author. Table 5 gives global statistics for residuals of the simultaneous fit. For completeness, the statistics obtained with the same second order parameters for the (dyad-g.s.) transitions data are presented in Table 6. To estimate the relative importance of the ten hot bands, a calculation extrapolated to $J_{max} = 20$ was achieved and the resulting sums of strengths are reported in Table 7.

<div align="center">DISCUSSION</div>

1. Comparison with previous results (in polyad scheme)

As expected, the second order dyad parameters, resulting from the same 1206 data are only slightly different than those published in Ref. (1.1); statistics and individual deviations are also equivalent, Setting to zero the statistically non significative parameter p_5 dots not change the situation, Rather, these very small variations come from the different schemes for weighting the data and for the least square method. It should be mentioned here that the signs of the parameters p_2 and p_3 (in $1(1,F_1)$) have been changed , by convention, in order to have coherent phase factors in the tetrahedral formalism. Direct comparison with the (pentad-dyad) parameters given in Ouardi's thesis (Table 5.c. 1 in Ref. (18)) is more difficult because numerous new data have been introduced in the present work and because the energy level basis of the t wo studies are significatively different

for the pentad states. The present work is based on the recent reanalyzes of the pentad energies with a fourth order Hamiltonian where ambiguities have been reduced completely to third order and partially to fourth order. As explained and illustrated in the d yad case by Qasri (22) and Perevalov *et al* (8), the contact transformations results in different values of the effective dipole parameters So, it should be emphasized that the set of parameters given in Table 4 cannot be separated from the Hamiltonian parameters of Ref. (20) used to calculate energy levels in the dyad and the pentad polyads.

2. *Comparison with previous isolated-band studies*

It is also very interesting to compare the present values with those resulting from numerical studies of isolated hot bands v_3-v_2 (k?) and v_3-v_4 (12) , even if the data are not exactly the same The main dipole parameter for v_3-v_2 in Ref. (14) is $\mu_{2,3}=-3.13\,10^{-2}$ D to be compared with the corresponding first order parameter $p_8=-3.31\,1\,0^{-3}$ D. For v_3-v_4 , in Ref. (12) one find $\mu_{3,4}=4.046\,10^{"}2$ D instead of the present $p_9=2,4297\,10^{"}2$ D. In both cases, differences are mainly due to the choice of scheme (isolated band rather than polyad), and in both cases the integrated band strengths in Table 7 are within a few percent of the previous values. From the theoretical study of Lotte (13), the expressions of these parameters are different for the t wo schemes (See also Table 10 of Ref. (13)):

$$\tilde{\mu}_{2,3} = -\frac{\sqrt{3}}{2}\mu_{23} + \frac{\mu_3}{\sqrt{2}}\left(\sqrt{2}\frac{t_{2,33}}{2\omega_3 - \omega_2} - \frac{t_{3,23}}{\omega_2}\right) + \frac{\mu_4}{\sqrt{2}}\left(-\frac{t_{2,34}}{\omega_3 + \omega_4 - \omega_2} - \frac{t_{3,24}}{\omega_2 + \omega_4 - \omega_3}\right) \quad [10]$$

$$\tilde{\mu}_{3,4} \cdot -\frac{\sqrt{6}}{2}\mu_{34}\frac{1}{\sqrt{2}}\left(\frac{\mu_3}{2\omega}2\sqrt{2}\frac{t_{4,33}}{(3)_4\omega_4} - \right)3 + 3\frac{\mu_4}{\sqrt{2}}\left(+\frac{\mu_4}{2\omega_4} - \sqrt{2}\frac{t_{3,44} - t_{4,34}}{\omega_3}\frac{}{\omega_3}\right) \quad [11]$$

In Eq. [1 0-11], μ are dipole moment first (p,) or second (μ_{ij}) derivatives, ω are fundamental frequencies and t are Hamiltonian tetrahedral parameters whose expressions in function of cubic

field constants are given in Table 6 of Ref. (13). The two last parenthesis contain resonant denominators (in $\omega_2 + \omega_4 - \omega_3$ or $2\omega_4 - \omega_3$) arrd the corresponding factors must be suppressed if the polyad scheme is used. An interesting consequence of the comparison of the numerical values obtained separately in both schemes is the possibility y of an estimation of the cubic coefficients of the nuclear potential of the molecule. Nevertheless, this estimation don't result so easily from Eqs. [10] or [11] because it requires a careful examination of the implicit contact transformations done in both schemes.

3. Success of the zero, first and second order expansions for (pentad-dyad) intensities

Since the zero order model for the dipole moment is definitively inadequate, one can compare advantages and drawbacks of first and second order models, relative to the needs of possible applications, The relative rrns of the (dyad - g.s.) tit change significantly from 6.5% to 3.0% by increasing the parameters from 3 to 7. The (pentad-dyad) tit improves from 21,59+. to 5.0% with the adjustment of 2 1 additional parameters (from 6 to 27) but this large improvment is mainly duc to the weakest bands, Nevertheless, the first order model with only six parameters can give a very useful prediction of hot band intensities. Moreover, it can be seen in Table 4 that second order parameters are not very accurately determined. The first order model is also interesting for further extrapolations: if onc consider the infrared transitions of the (P_n-P_{n-1}) system, where the P_n polyad contains all vibrational levels such as $n = n_b + 2n_s$, with n_b (n_s) respectively the numbers of bending (stretching) modes, the first order dipole moment development available for all these transitions (for $n \geq 2$) is exactly the same as for (P_2-P_1). This means that, to first order of approximation, the strengths of any infrared transition of the cascade (P_n-P_{n-1}) can be estimated with a reasonable precision from parameters given in Table 3 On the contrary, second order development needs new operators with unknown parameters. This property of first order

development has already been used to identify (octad-pentad) and possible (tetradecad-octad) lines appearing in jets of heated methane (23). More, the good prediction of their strengths provides a way to estimate the populations of the corresponding excited levels in this situation of non-equilibrium and then to obtain informations about relaxation process in the jets (24). Even at room temperature, some very weak lines of the octad-pentad (P_3-P_2) system have been clearly identified in a present FTS spectrum (1 O torr, 433 m), on the basis of a prediction made with these six parameters,

4. *Generalization to other hot bands of methane*

There are two infrared active fundamentals for the methane molecule, ν_3 and ν_4, and a second cascade of hot bands (P_n-P_{n-2}) with $n \geq 3$ can be associated to the (pentad-g.s.) transitions appearing in the 3pm region. The theoretical method described here is obviously available for the (octad-dyad) system. In this case, the first order dipole moment development contains only four parameters which are the same as those applying to the (pentad-g.s.) transitions; in other words, it is possible to estimate strengths of these hot bands from the pentad parameters as given in Table 3 of Ref. (20) and the same is true for higher hot bands in the (P_n-P_{n-2}) cascade, Concerning the second order development, as in the (pentad-dyad) case, the parameters associated with $\nu_2 + \nu_3-\nu_2$ and $\nu_3 + \nu_4-\nu_4$ are not linearly independent from the main μ_3 parameter so that the different methods presented here can be applied to the (octad-dyad) system. Preliminary numerical results (25) lead to the same kind of conclusions as in the present work and a complete analysis of these hot bands will be published elsewhere.

5. *Connection with the nuclear potential*

'J'he relations connecting the effective dipole moment parameters with the dipole derivatives and the nuclear potential coefficients have been recalled in Eqs. [10- 11] for the parameters $\tilde{\mu}_{2,3}$ and $\tilde{\mu}_{3,4}$ and for isolated band or polyad model. The same kind of relations have been written in Ref. (13) for the effective parameters $\tilde{\mu}_{0,23}$ and $\tilde{\mu}_{0,34}$ which are the main parameters for isolated bands $\nu_2 + \nu_3$ and $\nu_3 + \nu_4$ or two of the main parameters of the (octad-g.s.) system. This means that if the potential and dipole derivatives are known, it is possible to estimate hot band parameters from combination band ones and *vice versa,* as was seen in Ref. (14) and as was used previously for the (dyad-dyad) parameters (15,16). Other expressions involving quartic potential coefficient exist for instance for the effective parameters p_{25}, p_{26}, p_{27} (of the form $\mu_{4,44}$) and the parameters $\mu_{0,444}$ associated with $3\nu_4$. Then the determination of all dipole parameters provides informations on the quartic nuclear potential, Reciprocally, if the potential can be known, for instance from *ab initio* calculations, an estimation of some octad parameters is possible from the hot band ones.

6. *General studies of methane hot bands .*

The modelization of hot band strengths leads to predictions of hot band spectra which are not negligible, even in room temperature conditions. These predictions have evident applications in atmospheric physic or astrophysics (red stars for example), Other applications concern situations where hot methane is involved such as spectroscopy of heated jets, of plasmas containing methane or emission spectroscopy. To illustrate the fact that absorbance due to hot bands cannot be neglected, Table 8 gives the sums of calculated strengths for the first $(P_n - P_{n-1})$ systems at temperatures of 200, 296, 1000 and 2000 K. To obtain these sums, complete line by line predictions were made with Hamiltonian parameters of Refs. (19,20.25), respectively for the dyad, pentad and octad and a rough extrapolation in the tetradecad case. Concerning intensity, second order

parameters of Table 4 were used for the (dyad-g.s.) and (pentad-dyad) systems wheras estimation of strengths of upper hot bands were obtained from those of Table 3 (first order). At 1000 K, it can be seen, for example that the total contribution of the (pentad-dyad) system has the same order of magnit ude as the (dyad-g. s.) one and that the (octad-pentad) system is far for negligeable (one third), Available predictions in any chosen conditions can be obtained from the T.D.S. package (26), or by simple request to authors. At this point, it can be noticed that in absence of quantitative study of its own spectrum, the obtained parameters can be applied to the $^{13}CH_4$ molecule as a first approximation, Identification of hot lines has by itself spectroscopic interest in so far as only F_2 sublevels are infrared act ive from ground state, For example, (pentad-d yad) assignments have been used fbr the study of the pentad levels. In this case, transitions between sublevels A_1 and E of $2v_4$ and the fundamental level v4 (F_2) are allowed with not too weak intensities whereas transitions towards the ground state are forbidden by symmetry. Then hot band transitions frequencies were fitted together with infrared or Raman (pentad-g.s.) lines in the recent reanalysis of the pentad (20). Obviously, to obtain reliable identifications, a preliminary modelization of intensities is very important because there are no clear selection rules or regular structures in most of the methane spectra.

CONCLUSION

The three methods proposed to analyze hot band lines with oi without the cxx-responding dyad lines lead to results of comparable quality. The simultaneous fit method resulting in only one parameter set is the most satisfactory from the theoretical point of view. In particular, to first order, with only six intensity parameters, it is possible to predict with a reasonable accuracy (1 0°/0) the strengths of the strongest lines in the hot band cascade associated to the d yad. If higher precision is

needed, the second order model, with 27 intensity parameters, allows a prediction of the (dyad-g.s.) and (pentad-dyad) linestrengths with an accuracy of the order of 3% and 5%, respectively.

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Table Captions

Table 1: List of the (Pentad-Dyad) dipole moment operators

$(^a)$: Order of magnitude.

$(^b)$: Rotational-vibrational composition,

$\#1\text{-}7$ are parts of $\mu_{\{G.S.,Dyad\}}^{(Dyad,Pentad)}$ #8-27 are parts of $\mu_{\{Dyad,Pentad\}}^{(Dyad,Pentad)}$

Table 2: Reduced Matrix Elements of some vibrational operators of the (Pentad-Dyad) dipole moment

In front of each matrix arc given the characteristics ($\{n_s\},\Gamma_1;\{m_s\},\Gamma_2;\Gamma_v$) of the vibrational operator, then the numb-w(s) (from Table 1) of the rovibrational operator(s) where it appears.

Table 3: The first order dipole development

$(^a)$: Index of the corresponding parameter in Table 1. (*): fixed value.

σ : weighted standard deviation (See text). % :r.m.s. based on $(S_{exp}\text{-}S_{calc})/S_{exp}$

σ or % between parenthesis were obtained *aposteriori*.

Table 4 : The second order dipole moment development

(') : Index of the corresponding parameter in Table 1. (*): fixed value. (**): fixed to O for statistical reason.

σ : weighted standard deviation (See text). % : r.m.s. based on $(S_{exp}\text{-}S_{calc})/S_{exp}$.

σ or % between parenthesis were obtained *aposteriori*.

Table 5:   Statistics, by J and by band of the fit of (Pentad-Dyad) Strengths

^{0}/0 is the rms based on $(S_{exp}-S_{calc})/S_{exp}$.

These statistics correspond to the simultaneous fit of (dyad-g.s.) and (pentad-dyad).

Table 6:   Statistics, by J and by band of the fit of Dyad Strengths

%is therms based on $(S_{exp}-S_{calc})/S_{exp}$.

These statistics correspond to the simultaneous fit of (dyad-g.s.) and (pentad-dyad).

Table 7:   Sum of Strengths of the different $^{12}CH_4$ bands in the 5-1 0μm region

Sums (in $cm^{-2} atm^{-1}$ at 296 K) result from a calculation up to $J_{sup}=20$ for hot bands and from an extrapolation to $J_{sup}=30$ for the (d yad-g. s.) transitions.

Approximate band centers are obtained from fundamentals (calculated J=O levels).

Table 8:   Sums of strengths of the 5-1 0μm hot band cascade

Sum of strengths (in $cm^{-2} atm^{-1}$ at T) were calculated for the given maximum value of J_{sup}

Table 1:   list of the (Pentad-Dyad) dipole moment operators

i	$\Omega(K,\Gamma)$	n_s,Γ_1	m_s,Γ_2	r_v	(a)	(b)
Dyad parameters						
1	0(0,A₁)	0000A₁	0001F₂	F2	O	q
2	1(1,F₁)	0000A₁	0001F₂	F₂	1	Pq
3	1(1,F1)	0000A1	0100E	E	1	$P\ q$
4	2(2,F₂)	0000A₁	0100E	E	2	P^2q
5	2(0,A₁)	0000A₁	0001F₂	F2	2	P^2q
6	2(2,E)	0000A₁	0001F₂	F2	2	P^2q
7	2(2,F₂)	0000A₁	0001F₂	F2	2	P^2q
Hot Band arameters						
8	OOA	0100E . .	00 10F2	F₂	1	q^2
9	oOA	0001 F₂	1000A₁	F₂	1	q^2
10	0(0,A₁	0001F2	00 10F2	F₂	1	q^2
11	1(1,F₁)	0100E	1000A₁	E	2	Pq^2
12	1(1,F₁)	0100E	0010F₂	F₁	2	Pq^2
13	1(1,F₁)	0100E	0010F₂	F₂	2	Pq^2
14	1(1,F₁)	0001F₂	1000A₁	F₂	2	Pq^2
15	1(1,F₁)	0001F₂	0010F₂	F₁	2	Pq^2
16	1(1,F₁)	0001F₂	0010F₂	E	2	Pq^2
17	1(1,F₁)	0001F₂	0010F₂	F₂	2	Pq^2
18	0(0,A₁)	0100E	0101F₁	F₂	2	q^3
19	0(0,A₁)	0100E	0101F₂	F₂	2	q^3
20	0(0,A₁)	0100E	0002F₂	F₂	2	q^3
21	0(0,A₁)	0001F₂	0200A₁	F₂	2	q^3
22	0(0,A₁)	0001F₂	0200E	F₂	2	q^3
23	0(0,A₁)	0001F₂	0101F₁	F₂	2	q^3
24	0(0,A₁)	0001F₂	0101F₂	F₂	2	q^3
25	0(0,A₁)	0001F₂	0002A₁	F₂	2	q^3
26	0(0,A₁)	0001F₂	0002E	F₂	2	q^3
27	0(0,A₁)	0001F₂	0002F₂	F₂	2	q^3

(ᵃ): Order of magnitude,
(ᵇ): Rotational-vibrational composition

#1-7 arc parts of $\mu_{\{G.S ,Dyad\}}^{(Dyad,Pentad)}$

#8-27 are parts of $\mu_{\{Dyad,Pentad\}}^{(Dyad, Pentad)}$

Table 2: Reduced Matrix Elements of some vibrational operators of the (Pentad-Dyad) dipole moment

(Schematic Shape)

	$v,$	v_3	$2v_2$		$v_2 + v_4$		$2v_4$		
	Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
v_2									
v_4									

0100 E; 0101 F_2; F_2   *18*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	0	0	0

0100 E; 0101 F_2;F_2   *19*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
o	0	0	0	0	1	0	0	0
0	0	0	0	0	0	0	0	0

0001 F_2; 0002 A_1; F_2   *25*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	o	0	0	0	0	0	0
0	0	0	0	0	0	-1	0	0

0001 F_2; 0002 E;F_2   *26*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0

0001 F_2; 0002 F_2;F_2   *27*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	1

0000 Al; 0001 F_2; F_2   *1,2,5,6*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	0	0	1	1	0	0	0
0	0	0	0	0	0	$-\sqrt{2/3}$	$-2/\sqrt{3}$	$-\sqrt{2}$

(WOO Al; 0100 E; E   *3,4*

Al	F_2	Al	E	F_1	F_2	A_1	E	F_2
0	0	-1	$-\sqrt{2}$	0	0	0	0	0
0	0	o	0	$-\sqrt{3/2}$	$+\sqrt{3/2}$	0	0	0

In front of each matrix arc given the characteristics ($\{n, \}$,Γ_1;$\{m_s\}$),Γ_2;Γ_v) of the vibrational operator, then the number(s) (from Table 1) of the rovibrational operator(s) where it appears.

Table 3   The first order dipole development

(a)	Unit	Dyad	Pentad-Dyad (extrapol)	Pentad-Dyad (direct)	Simult.
Dyad Parameters					
1	10^{-2}D	9.798(12)	9.79835(*)	10.110(50)	9.862(18)
2	10^{-5}D	7.82(63)	7.81799(*)	30.2(2.1)	13.27(93)
3	10^{4}D	1.390(13)	1.38969(*)	1.735(87)	1,402(22)
Pentad-Dyad Parameters					
8	10^{3}D	I	-5.62(20)	-4.92(24)	-5.49(17)
9	10^{2}D	/	3.2394(61)	3.331(15)	3.2600(71)
10	10^{-2}D	/	2.346(15)	2.299(17)	2.337(13)
σ(d-g 1206)	8.4		(8.4)	(20.7)	9.1
%(d-g 1206)	6.5		(6.5)	(11.4)	6.5
σ(p-d 1732)	(868)		40.7	40.2	40.5
%(p-d 1732)	(591)		21.8	21.0	21,5
%(p-d 1634)	(605)		13.0	11.6	12,5

(a) : Index of the corresponding parameter in Table 1. (*) : fixed value.

σ : weighted standard deviation (See text), % : R.M.S. based on $(S_{eq}-S_{calc})/S_{eq}$, σ or % between parenthesis were obtained *aposteriori*.

Table 4   The second order dipole moment development

(a)	Unit	Dyad	Pentad-Dyad (extrapol.)	Pentad-Dyad (effective)	Simult.
Dyad Parameters					
1	10^{-2}D	9.8361(57)	9.83609(*)	0.0(*)	9.8549(80)
2	10^{-4}D	2.568(38)	2.56806(*)	2.56806(*)	2.519(40)
3	10^{-4}D	1.6104(88)	1.61041(*)	1.61041(*)	1.6211(88)
4	10^{-6}D	2.524(44)	2.52408(*)	2.52408(*)	2.551(45)
5	10^{-7}D	0.0(**)	0.0(**)	0.0(**)	4.7(1.7)
6	10^{-7}D	8.2(1.1)	8.16001(*)	8.16001(*)	6.9(1.1)
7	10^{-6}D	-3.08(14)	-3.08428(*)	-3.08428(*)	-3.19(14)
Pentad-Dyad Parameters					
8	10^{3}D	/	-3.75(15)	-3.75(15)	-3.31(13)
9	10^{2}D	' 1	2.4829(83)	2.4829(83)	2.4297(74)
10	10^{-2}D	/	2.2033(52)	2,2033(52)	2,1973(45)
11	10^{5}D	I	4.93(56)	4.93(56)	5.31(48)
12	10-SD	—1	7.54(56)	7.54(56)	7.36(49)
13	110-5D	/	3.10(56)	3.10(56)	3.04(50)
14	10^{-5}D	/	9.56(20)	9.56(20)	9.22(21)
15	10^{5}D	/	7,80(37)	7.80(37)	7.93(32)
16	10^{-5}D	)	8.69(32)	8.69(32)	8,70(28)
17	10^{5}D	/	-4.83(41)	-4,83(41)	-4.46(36)
18	10^{-2}D	/	1.5(2.4)	985.1(2.4)	12.3(21)
19	10^{-3}D	/	5.98(22)	104.34(22)	6.02(20)
20	10^{-3}D	I	1.6(1.0)	1.6(1.0)	4,44(88)
21	10^{-4}D	/	8,78(93.)	8,78(93.)	-35.17(66)
22	10^{-3}D	/	-2.655(17)	-2.655(17)	-2.653(15)
23	10^{-4}D	/	-8.65(57)	-8.65(57)	-4.06(50)
24	10^{-4}D	/	-3.90(45)	-3.90(45)	-4.02(39)
25	10^{-3}D	/	-5.98(23)	-86.29(23)	-4.02(21)
26	10^{-4}D	/	-6.5(1.9)	-1142.2(1.9)	-8.5(1.8)
27	10^{-3}D	/	-6.67(22)	-145.77(22)	-6.96(20)
σ(d-g 1206)		4.49	(4.49)	(4.49)	4.6
%(d-g 1206)		3.0	(3.0)	(3.0)	3.0
σ(p-d 1732)		(880)	8.0	8.0	6.6
%(p-d 1732)		(598)	5,8	5.8	5.0

(') : Index of the corresponding parameter in Table 1. (*) fixed value,
(**) : fixed to O for statistical reason,

σ : weighted standard deviation (See text), % : r.m.s. bawd on
$(S_{eq}-S_{calc})/S_{eq}$, σ or% between parenthesis were obtained *aposteriori*.

Table 5: Statistics, by J and by band of the fit of (Pentad-Dyad) Strengths

J(sup)	ν_1-ν_2		ν_1-ν_4		ν_3-ν_2		ν_3-ν_4		2ν_2-ν_2	
	n	%	n	%	n	%0	n	%0	n	%
0	/	/	/	/	/	/	I	/	/	/
1	/	/	/	/	5	2.2	7	3.9	/	/
2	/	/	/	/	12	2.1	16	3.6	1	1.3
3	/	/	6	4.2	18	3.3	36	3.6	/	/
4	/	/	6	1.8	24	2.9	40	4.0	5	4.9
5	1	4.3	6	2.4	18	3.3	64	4.1	7	4,8
6	2	2.1	14	3.8	27	3.9	74	3.7	9	4.5
7	5	2.7	10	5.0	32	4.9	76	4.6	14	6.0
8	1	8.4	10	6.0	28	4.7	91	4.5	13	4,7
9	1	5.5	4	6.3	28	4.2	79	4.5	5	4.5
10	/	/	7	4.9	25	4.7	71	5.3	1	11.0
11	/	/	8	6.3	24	5.9	41	6.1	2	8.1
12	/	/	2	7.7	17	6.0	35	6.5	I	/
13	/	/	/		16	7.7	30	7.6	/	/
14	1	2.2	1	7'0	8	5.0	19	7.6	1	1.7
15	/	/	/	/	3	5.3	9	6.1	/	/
16	/	/	/	/	/	/	3	7.1	/	/
Total	11	3.9	74	4.9	285	4.7	691	5.0	58	5.3

(sup)	2ν_2-ν_4		ν_2+ν_4-ν_2		ν_2+ν_4-ν_4		2ν_4-ν_4		All	
	n	%	n	%	n	%	n	0/0	n	0/0
0	/	/	/		/		1	1.0	1	1.0
1	2	5.5	1	3'3	1	8'6	3	3.5	17	3.8
2	2	6.3	1	3.2	3	6.7	7	2.1	42	3.4
3	6	3.9	10	4.3	8	5.3	23	4.7	103	4.2
4	9	4.7	8	4.2	9	4.3	17	3.6	115	3.7
5	10	3.9	12	4.8	16	4.6	30	4.7	163	4.3
6	11	6.9	11	5.6	16	5.1	41	4.4	204	4.2
7	13	4.1	12	4.9	17	4.7	27	4.4	204	4.9
8	9	4.2	8	5.4	18	5.3	33	4.3	215	4.7
9	10	6.1	10	7.3	19	6.4	33	4.7	188	5.()
10	10	6.2	4	5.0	8	7.0	34	5.4	160	5.4
11	10	7.3	3	3.4	8	5.9	13	5,7	109	6.0
12	I	/	2	3.0	3	6.1	11	5.8	80	6.4
13	I	/	5	7.5	1	11.1	8	4.6	60	7.4
14	/	/	2	6.7	1	0.7	9	6.1	42	6.5
15	/	/	2	7.6	1	8.8	8	5.4	23	6.0
16	/	/		11.0	/	/	2	6.2	6	7 6
Total	92	5.5	92	5.5	129	5.6	300	4.7	1732	5.0

% is the rms based on $(S_{exp}-S_{calc})/S_{exp}$.
These statistics correspond to the simultaneous fit of (dyad-g.s.) and (pentad-dyad).

Table 6:   Statistics, by J and by band of the fit of Dyad
                              Strengths

ν_2			$v4$			Dyad		
Js	n	%0	Js	n	%	Js	n	%
0	/	/	0	1	1.5	0	1	1.5
1	1	0.4	1	4	0.9	1	5	0.8
2	3	0.9	2	7	1.4	2	10	1.3
3	9	2.9	3	11	1.8	33	20	2.4
4	16	2.3	4	15	2.0	4	31	2.2
5	22	2.3	5	27	2.1	5	49	2.2
6	24	1.9	6	32	2.2	6	56	2.1
7	32	2.3	7	46	2.2	7	78	2,3
8	37	2.3	8	53	2.7	8	90	2.6
9	30	2.6	9	65	2.6	9	95	2.6
10	32	3.S	10	65	2.4	10	97	2,8
11	42	3.7	11	68	3.0	11	110	3.3
12	38	3.5	12	75	2.5	12	113	2.9
13	40	2.9	13	63	3.3	13	103	3.1
14	29	2.1	14	43	3.3	14	72	2.9
15	38	3.S	15	39	2.9	15	77	3,2
16	27	3.5	16	35	3.6	16	62	3.5
17	15	2.2	17	29	5.2	17	44	4.4
18	7	4.6	18	26	2.8	18	33	3.3
19	4	5.0	19	22	3.6	19	26	3.9
20	I	I	20	16	3.1	20	16	3.1
21	/	/	21	11	3.0	21	11	3.0
22	/	/	22	5	4.5	22	5	4.5
23	/	/	23	2	6.0	23	2	6.0
All	446	3.0	All	760	2.9	All	1206	3.0

%0 is the rms based on $(S_{eq}-S_{calc})/S_{eq}$. These statistics
correspond to the simultaneous fit of (dyad-g.s.) and
(pentad-dyad).

Table 7   Sum of Strengths of the different $^{12}CH_4$ bands in the 5-10μm region

Band	Center (cm^{-1})	Sum of strengths
$\nu_1 - \nu_4$	1607	$6.89\ 10^{-4}$
$\nu_1 - \nu_2$	1384	$8.75\ 10^{-4}$
$\nu_3 - \nu_4$	1710	$4.81\ 10^{-2}$
$\nu_3 - \nu_2$	1485	8.7110^{3}-
$2\nu_2 - \nu_4$	1750	5.00104
$2\nu_2 - \nu_2$	1533	2.6610-3
$\nu_2 + \nu_4 - \nu_4$	1533	$8.72\ 10^{-}$
$\nu_2 + \nu_4 - \nu_2$	1310	$1.45\ 10^{-1}$
$2\nu_4 - V4$	1310	9.3110-'
$2\nu_4 - \nu_2$	1087	$7.67\ 10^{-5}$
All hot bands	/	1.15
ν_2	1533	1.35
ν_4	1310	126.2
Dyad	/	127.6

Sums (in $cm^{-2} atm^{-1}$ at 296 K) result from a
calculation up to $J_{max}=20$ for hot bands and from
an extrapolation to $J_{max}=30$ for the (dyad-g.s.)
transitions,
Approximate Band Centers are obtained from
fundamentals (calculated J=0 levels).

Table 8:   Sums of strengths of the 5-10μm hot band cascade

Temperature (K)	Dyad-G.S. ($J \leq 30$)	Pentad-Dyad ($J \leq 20$)	Octad-Pentad ($J \leq 14$)	Tetradecad-Octad ($J \leq 7$)
200	190.0	7.610-	$2.416\,10^7$	$\leq 10^{-6}$
296	127.4	1.15	$5.47\,10^3$	$\leq 10^{-6}$
1000	14.64	12.34	4.98	$6.06\,10^{-1}$
2000	$6,60\,10^{-1}$	$1.14_{\,2}$	$9.51\,10^1$	$2.34\,10^{-1}$

Sums of strengths (in $cm^{-2}atm^{-1}$ at T) were calculated for the given maximum value of J_{max}.